ARCHIVES
of
FOUNDRY ENGINEERING

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (1897-3310)
Volume 14
Issue 3/2014

11 – 16

2/3

The Influence of Chemical Surface Treatment on the Corrosion Resistance of Titanium Castings Used in Dental Prosthetics

B. Burnat [a], M. Parchańska-Kowalik [b], L. Klimek [b,] *
[a] University of Lodz, Department of Electroanalysis and Electrochemistry, Tamka 12, 91-403 Lodz, Poland
[b] Medical University of Lodz, Department of General Dentistry, Chair of Dental Technique,
Pomorska 251, 92-213 Lodz, Poland
*Corresponding author. E-mail address: leszek.klimek@p.lodz.pl

Received 30.04.2014; accepted in revised form 15.05.2014

Abstract

Air abrasion process is used for cleaning casting surface of prosthetic components, and to prepare the surface of these elements for the application of veneering items. Its side effect, however, is that abrasive particles are embedded in the treated surface, which can be up to 30% of the surface and it constitutes the side effect of this procedure. Such a significant participation of foreign material can not be indifferent to the properties of the surface. Embedded particles can be the place of stress concentration causing cracking of ceramics, and may deteriorate corrosion resistance by forming corrosive microlinks. In the latter cases, it would be advisable to remove elements embedded into the surface. The simplest method is chemical etching or electrochemical one. Nevertheless, these procedures should not significantly change the parameters of the surface. Among many possible reagents only a few fulfills all the above conditions. In addition, processing should not impair corrosion resistance of titanium, which is one of the most important factors determining its use as a prosthetic restoration in the mouth. The study presented results of corrosion resistance of titanium used to make prosthetic components by means of casting method, which were subjected to chemical processing designed to remove the embedded abrasive particles. The aim of the study was to investigate whether etching with selected reagents affects the corrosion resistance of titanium castings. For etching the following reagents were used: 30% HNO_3 + 3% HF + H_2O, HNO_3+ HF+ glycerol (1:2:3), 4% HF in H_2O_2, 4% HF in H_2O, with a control sandblasted sample, not subjected to etching. Tests demonstrated that the etching affected corrosion properties of test samples, in each case the reduction of the corrosion potential occurred - possibly due to the removal of particles of Al_2O_3 from the surface and activation of the surface. None of the samples underwent pitting corrosion as a result of polarization to 9 V. Values of the polarization resistance, and potentiodynamic characteristics indicated that the best corrosion resistance exhibited the samples after etching in a mixture of 4% solution of HF in H_2O_2. They showed very good passivation of the surface.

Keywords: Titanium castings, Prosthetic components, Abrasive blasting, Chemical treatment, Corrosion tests

1. Introduction

Titanium is a metal material that has been used in dentistry and medicine for many years and its application and popularity continues to grow [1-4]. This is due to its unique characteristics that are unparalleled to other available metals and alloys, these are predominantly its good corrosion resistance and biocompatibility [1,3,4,5,6]. Thanks to these features titanium has been successfully employed for many years in dentistry. Its use in dental prosthetics is invaluable, as apart from the above-mentioned implants there is also a possibility of fabricating of titanium, and in the laboratory conditions, almost all prosthetic constructions. These are both fixed elements like crown-root inlays, onlays, crowns and bridges, as well as mobile ones in the form of frameworks of partial dentures.

Due to the corrosion resistance, it is possible to eliminate harmful for the body phenomenon of transition of metal ions to the tissues, which in conditions of the oral cavity is of great importance. Another advantage of titanium is its low density, which is 4.51 g/cm^3, and for restorations is an undeniable asset. Other characteristics relevant to the prosthetic application are: low thermal conductivity (it is 14 times smaller than in gold alloys), no allergic reactions, non-toxicity, as a result of passivation of titanium oxides, absence of taste sensations and relatively low price (compared to the price of platinum or gold) [1,7].

Nevertheless, in addition to many benefits titanium has also disadvantages such as high affinity for oxygen, which causes its oxidation, especially at higher temperatures. An important problem is its processing under laboratory conditions, in particular, the problem with the implementation of castings due to titanium's strong oxidation at high temperature. The ensuing consequence of the above- mentioned adverse events and technical difficulties is the fact that casting titanium and its alloys by means of lost wax casting is very difficult. Therefore, to meet demands of modern dental prosthetics, special casting techniques are use [1,7]. Induction melting with the use of pressure - vacuum system, which is composed of two chambers, is the most frequently employed. The first of the chambers serves for melting in argon shield and the other – vacuum holds a casting mold.

In the execution of dental crowns and bridges on the frame of titanium, difficulty in titanium processing is not the only problem. The combination of titanium with dental ceramics also poses some problems due to specific nature of the titanium surface. Metal-ceramic connection is a place of many factors. These are: the influence of the van der Waals force, mechanical anchoring resulting from expansion of a metal surface (e.g. by abrasive blasting), compressive stresses associated with differential shrinkage of metal and ceramics and a chemical bond formed between porcelain and the oxide layer during oxidation, which most frequently occurs before firing of porcelain [1,8,9].

The main problem in the combination of titanium and ceramics is its high propensity to passivation that is, forming a layer of titanium oxide (mainly TiO_2) under the effect of high temperatures. While in the case of prosthetic components made from other alloys such as Ni-Cr or Co-Cr the obtained oxide film is relatively thin and provides a chemical bond of ceramics with oxide layer, when it comes to titanium oxidation takes place too rapidly and there are great difficulties in its controllable acquisition, thus, resulting passive layer is too thick, which causes problems to fuse it with ceramics. Although low melting point ceramics that have been developed in recent years provide a suitable thickness of the oxide layer, still, the strength of ceramic fused to titanium is insufficient nowadays and only slightly greater than the minimum required for metal-ceramic bonds recommended by ISO [1,7,10,11].

In the case of metal substructures made of titanium, to enhance the bond strength of the metal to dental ceramic abrasive blasting is commonly used. It is currently the only way to improve the quality of these bonds. Studies have demonstrated that unblasted metal surface does not provide a sufficient bonding of metal to ceramics [12]. Abrasive blasting improves the bond strength of metal to ceramic, as it causes the formation of surface irregularities and, thus increases its roughness. This, in turn, improves mechanical retention and wetting of metal frame to porcelain surface [1,13,14]. Blasting is undoubtedly a necessary process in the course of processing prosthetic metal-porcelain elements, but apart from the above mentioned benefits, it also has some adverse effect. The studies conducted to date have shown that after blasting on the surface of titanium remain embedded abrasive grains [15,16]. This is caused by both high kinetic energy of the grains hitting the surface of the metal and relatively low hardness of titanium. The content of abrasive material particles increases with the power of applied pressure. Also grains size plays a role here - the larger a grain, the lower number of particles driven into. There are studies showing that the number of stuck particles is significant and according to different authors varies between 13 and 30% of the metal surface [15].

This phenomenon has a significant impact on the quality of titanium to dental ceramic bonding and it is detrimental, as it is a contamination of metal surface, which ceases to be homogeneous. This results in a reduction in mechanical anchoring of ceramics and the chemical inhibition of the bonding between porcelain and titanium oxides. Abrasive particles are so firmly anchored on the metal surface, that it is impossible to remove them by means of steam cleaning, which is standard procedure when fabricating prosthetic components. In addition, embedded elements can cause vulnerability of ceramics [17].

The problem of embedded particles of abrasive material may be the key to explain the reasons for poor bonding of ceramic to titanium substructure and therefore it becomes necessary to study techniques removing these contaminants, which will consequently improve ceramic to titanium bond strength [1,15,18,19]. Studies have shown that it is possible to remove these particles by means of chemical etching method [24]. It must be remembered, however, that the methods should not substantially change surface roughness and its other parameters relevant to its good quality of bonding with ceramics. Among many possible reagents only a few fulfills all the above conditions [24]. There remains to answer the question how far such a chemical treatment affects the corrosion resistance of titanium, which is one of the most important factors for its use as a prosthetic restoration in the mouth.

2. Materials and research methods

Tritan titanium discs CpTi 1 from Dentaurum with a diameter of 21 mm and a thickness of 5 mm were the research material. Minimum titanium content was of 99.5% with a trace amount of Fe, O, H, N, C in accordance to ASTM classification. In order to standardize the surface discs were polished successively with SiC abrasive papers of gradations 220, 400, 600 and 800. During that procedure water cooling was employed. After each polishing, the samples were rinsed and dried with compressed air. Prepared in this way discs were subjected to abrasive blasting with corundum grains with Mikroblast Duo.

The following processing parameters were used:
- Grain size of 110 microns,
- Working pressure of 0,4 MPa,
- Steam incident angle 45°,
- Working distance 10 mm.

After the treatment, the samples were cleaned with pressurized steam and dried with compressed air.

Prepared samples were divided into five groups intended for etching, including the control one. Each group was subjected to etching with a specific etching factor.
- Group 0 the control one: sandblasted, without etching,
- Group I: 30% aqueous solution of HNO_3 + 3% HF,
- Group II: 1 part by volume of HNO_3 + 2 parts by volume of HF + 3 parts by volume of glycerol,
- Group III: 4% solution of HF in H_2O_2,
- Group IV: 4% solution of HF in H_2O.

Reagents were chosen so as to minimally change parameters of the treated surface [24].

Etching was carried out in a suitable mixture in an ultrasonic bath for 3 minutes, rinsed with water and then purified in water in an ultrasonic bath for 10 min, dried with argon and conditioned for 15 min at 37°C. Prepared this way samples were subjected to the corrosion test.

3. Results

In order to determine the corrosion potential, the potential of the samples according to the reference electrode was recorded in an open circuit during 2000 s. Final stabilized potential was taken as the corrosion potential E_{cor}. Values of E_{cor} potential for titanium samples depending on the etching mixture are presented in Fig. 1. This figure also contains E_{cor} potential value of the control sample, i.e. without etching.

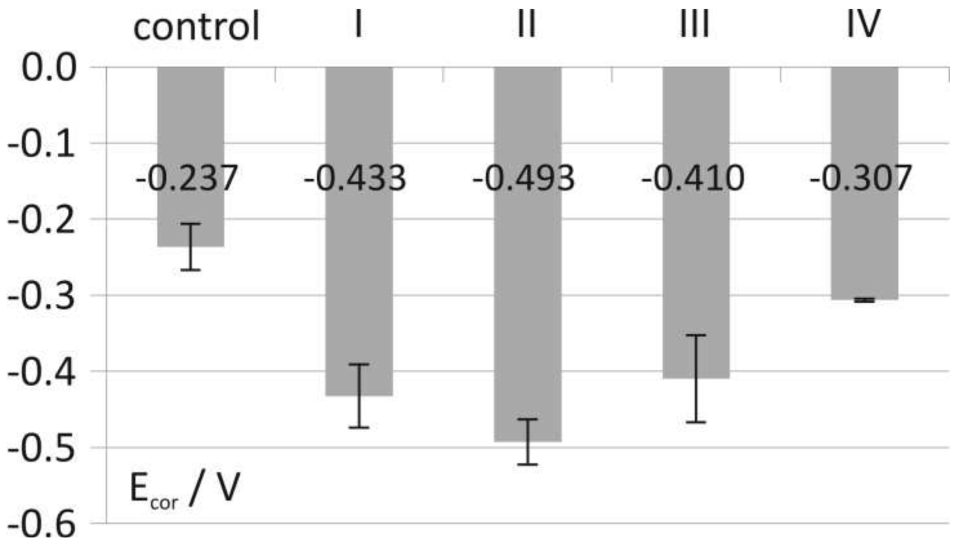

Fig. 1. Corrosion potential of chemically etched titanium samples

The sandblasted titanium samples (without chemical etching) have a corrosion potential value ca. -0.24 V. This value derives from the presence of thin TiO_2 layer due to spontaneously passivation of titanium and Al_2O_3 grains stuck on the titanium surface as a result of sandblasting [27]. These embedded corundum grains can be partially removed from the titanium surface by chemical etching [24]. The main component of the etching mixtures used for titanium samples is hydrofluoric acid (HF), which reacts with titanium forming soluble salts and thus releasing of alumina grains is possible. In the presence of oxidizing reagents (i.e. HNO_3, H_2O_2) additionally passivation of titanium is occurring. Any changes in the chemical composition of the surface due to the etching result in a change of the corrosion potential value. The etching of titanium surfaces in all mixtures of acids reduces the corrosion potential E_{cor} value (Fig. 1.). The greatest changes in the E_{cor} potential are observed for samples etched in mixture II (HNO_3 + HF + glycerol), whereas the weakest changes are observed in case of etching in mixture IV (HF +H_2O).

Polarization resistances R_p were determined by polarization of the samples in a typical potentiostatic connection in the potential range ±0.02 V versus determined E_{cor} potential. The results of R_p measurements are shown in Fig. 2.

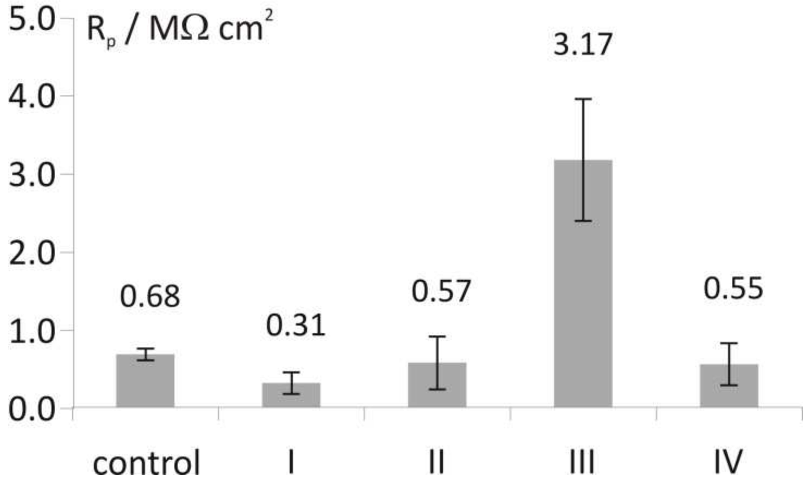

Fig. 2. Polarization resistance of chemically etched titanium samples

Polarization resistance of control sample (without etching) reaches a value of 0.68 MΩ·cm^2. The use of etching mixtures I, II and IV cause a decrease in the polarization resistance, while etching in mixture III greatly increases value of R_p. In general, a change in the resistance R_p may be due to changes in surface roughness as well as its reactivity. Lower values of the resistance R_p are connected with a higher roughness and/or reactivity of the surface. In turn, higher values of R_p may indicate lower surface roughness or lower reactivity of the material. Based on the polarization resistance value, a corrosion rate of the material may be estimated, and thus it is possible to compare the corrosion resistance of various samples. In this study the corrosion rate, in micrometers per year, was calculated according to formula (1) [28].

$$CR = \frac{K_1 \cdot EW \cdot B}{R_p \cdot \rho} \quad (1)$$

where:
CR-corrosion rate in μm/year,
constant K_1=3.27 μm·g/(μA·cm·year),
EW - equivalent weight for Ti (12.035),
B- Stern-Geary's coefficient (0.026, with the assumption of both anodic and cathodic Tafel constants of 0.12 V/decade),
R_p - polarization resistance in MΩ·cm^2
ρ- density of Ti (4.50 g/cm^3).

The values of the corrosion rate calculated for different variants of chemical etching of titanium samples are collected in Table 1.

Table 1.
Corrosion rate of chemically etched titanium samples

Etching mixture	CR (μm/year)
without etching	0.336
I	0.737
II	0.400
III	0.072
IV	0.413

The presented data clearly shows, that chemical etching of titanium samples has an effect on their corrosion rate. The etching in a mixture I (HNO_3 + HF) results in more than two-times higher corrosion rate in relation to the control sample (without etching). Whereas only slightly effects on the corrosion rate of the investigated samples may be observed in case of etching in mixture II (HNO_3 + HF + glycerol) and IV (HF+H_2O). The most favorable effect is observed for samples etched in mixture III (HF+H_2O_2) - titanium samples are characterized by the lowest value of corrosion rate (ca. 5 times lower in relation to control sample).

The potentiodynamic characteristics in a wide range of anodic polarization were performed from the potential of 0.2 V below E_{cor} to the potential of 9 V, next the direction of polarization was reversed and backward curve was registered. The obtained potentiodynamic characteristics of titanium samples after different chemical treatments are shown in Fig. 3. For better readability sections of return branches have been cut off.

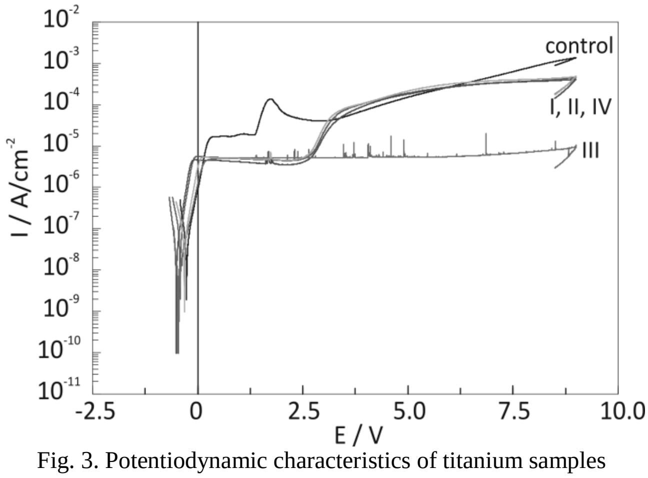

Fig. 3. Potentiodynamic characteristics of titanium samples (scan rate of 1 mV/s)

From all the types of investigated samples the highest reactivity presents the control sample. The potentiodynamic characteristic for this sample has a narrow passive range up to about 1.5 V. The current density in a passive range is in the order of $2 \cdot 10^{-5}$ A/cm^2. For samples etched in mixtures I, II and IV a passive range ends at potential of ca. 2.5 V. During further polarization the transpassivation process occurs. The sample etched in mixture III was totally passivated in whole polarization range. In this case, some current fluctuations were observed above the potential of 2 V.

None of the tested samples undergo pitting corrosion in whole polarization range. The backward curves are below the forward potentiodynamic curves, which means that only passivation of titanium samples occurred during anodic polarization. This result is in agreement with optical analysis of samples surfaces after anodic polarization - the surfaces changed color from silver to blue-violet or gold, but there was no corrosion pits.

4. Conclusions

1. The chemical etching of sandblasted titanium samples has an effect on their corrosion properties - in any case the lowering of corrosion potential was observed.
2. The values of polarization resistance, corrosion rate and potentiodynamic characteristics indicate that titanium samples etched in mixture containing 4% HF in H_2O_2 exhibit the best corrosion properties.

References

[1] Surowska, B. (2009). *Biomaterials metal and metal-to-ceramic dental applications*. Lublin: Ed. Lublin University of Technology.

[2] Marciniak, J. (2002). *Biomaterials*. Gliwice: Ed. Silesian University of Technology.

[3] Czarnowska, E., Krupa, D., Wierzchoń, T. (2004). *Surface Engineering of titanium in the manufacture of biomaterials*. Warszawa: Ed. Warsaw University of Technology.

[4] Lauterschlager, E.P. & Monaghan, P. (1993). Titanium and titanium alloys as dental materials. *Int. Dental of Journals.* 43(3), 245-253.

[5] Czarnowska, E., Wierzchoń, T. & Maranda-Niedbała, A. (1999). Properties of the surfaces layers on titanium alloy and their biocompatibility in in vitro tests. *J. Mater Process. Technol.* 92(1), 190-194.

[6] Niionomi, M. (1998). Mechanical properties of biomedical titanium alloys. *Material Sc. And Engineering A.* 243, 231-236.

[7] Orlicki, R. & Kłaptocz, B. (2005). Titanium and its alloys - properties, applications in dentistry and processing methods. In VI International Scientific Symposium Dental Engineering Biomaterials, 17-19 June 2005.

[8] Guo, L., Liu, X., Gao, J., Yang, J., Guo, T. & Zhu, Y. (2010). Effect of Surface Modifications on the Bonding Strength of Titanium–Porcelain. *Mater. Manuf. Processes* 25(8) 710-717.

[9] Majewski, S.W. (2005). *Reconstruction of teeth with fixed restorations*. Kraków: Ed. Foundation for the Development of Prosthodontics.

[10] Lin, M., Kuo-Lung, T., Sheng-Chieh, L. & Her-Hsiung, H. (2012). Bonding of dental porcelain to non-cast titanium with different surface treatments. *Dent. Mater. J.* 31(6), 933-940.

[11] ISO 9693-1999. Metalceramic dental restorative systems.

[12] Hajduga, M. & Barwikowska, D. (2007). The effect of sandblasting the surface of crowns on the quality of the connection with dental ceramics. *Modern Dental Technician.* 3, 40-45.

[13] Oshida, Y., Munoz, C.A., Winkler, M.M., Hashem, A. & Itoh, M. (1993). Fractal dimension analysis of aluminum oxide particle for sandblasting dental use. *Bio-Med. Mater. Eng.* 3(3), 117-126.

[14] Reyes, M.J.D., Oshida, Y., Andres, C.J., Barco, T., Hovijitra, S. & Brown, D. (2001). Titanium–porcelain system. Part III: Effects of surface modification on bond strengths. *Bio-Med. Mater. Eng.* 11(2), 117-136.

[15] Gołębiowski, M., Pietnicki, K. & Klimek, L. (2010). Influence of parameters of air abrasion on the number of abrasive particles embeddet in the surface of titanium alloy. *Dental Magazine*. 6, 34-38.

[16] Grajek, A. Lubas, M., Kotarski, T., Wieczorek, P. & Jasiński, J. (2008). The surface state and quality of joint metal ceramic after initial sand blasting. *Materials Engineering.* 6, 1082-1085.

[17] Van Niekerk, A.J., Ciaputa, T. (2007). *Modern dental restorations, art and crafts. Texts selected.* Katowice: Elamed.

[18] Cai, Z., Bunce, N., Nunn, M.E. & Okabe, T. (2001). Porcelain adherence to dental cast CP titanium: effects of surface modifications. *Biomaterials.* 22, 979-986.

[19] Al Jarabbi, Y.S., Zinelis, S. & Eliades, G. (2012). Effect of sandblasting conditions on alumina retention in representative dental alloys. *Dent. Mater. J.* 31(2), 249-255.

[20] Liu, X., Chu, P.K. & Ding, C. (2004). Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater. Sci. Eng.* 47(3), 49-121.

[21] Bandi, S., Chadalavada, D. & Kumar, A.S. (2012). Evaluation and comparison of surface modifications of commercially pure grade-I titanium by combination technique of blasting with alumina followed by acid etching and oxidation with NaOH. *Annals and Essences of Dentistr.* IV(4), 1-8.

[22] Darvell, B.W., Samman, N., Luk, W.K., Clark, R.K.F. & Tideman, H. (1995). Contamination of titanium castings by aluminium oxide blasting. *J. Dent.* 23(5), 319-322.

[23] Gołębiowski, M., Sobczak-Guzenda, A., Szymański, W. & Klimek, L. (2010). Influence of paraeters of stream abrasive treatment of titanium surfaces on contact angle and surfaces free energy. *Materials Engineering.* 4(173), 978-980.

[24] Parchańska-Kowalik, M. & Klimek, L. (2013). The influence of chemical processing on the condition of the titanium surface. *Materials Engineering.* 5(195), 526-529.

[25] Schiff, N., Dalard, F., Lissac, M., Morgon, L. & Grosgogeat, B. (2005). Corrosion resistance of three orthodontic brackets:

a comparative study of three fluoride mouthwashes. *European Journal of Orthodontics*. 27, 541-549.

[26] Klimek, L., Pierzynka, R., Błaszczyk, T., Burnat, B., Scholl, H. &Marciniak, S. (2009). The effect of recasting on corrosion of DUCINOX prosthetic alloy. *Archives of Foundry and Engineering.* 9(3), 67-70.

[27] Burnat, B., Walkowiak-Przybyło, M., Błaszczyk, T. & Klimek, L. (2013). Corrosion behaviour of polished and sandblasted titanium alloys in PBS solution. *Acta of Bioengineering and Biomechanics.* 15 (1), 87-95.

[28] Lian, T., Whalen, M.T., Wong, L. (2004). Corrosion Behavior of Titanium Grade 7 in Fluoride-Containing NaCl Brines. In 206th Electrochemical Society Fall Meeting Symposium Proceedings. 3-8 October 2004 (UCRL-CONF-207609). United States: Honolulu, HI.